THE POLAROGRAPHIC ANALYSIS OF ZINC IN THREE VARIETIES OF SOYBEANS

A THESIS

Submitted in partial fulfillment
of the requirements for the Degree
of Master of Science in Chemistry

by

William B. Satkowski

Georgia School of Technology
Atlanta, Georgia
1942

THE POLAROGRAPHIC ANALYSIS OF ZINC IN THREE VARIETIES OF SOYBEANS

Approved:

Date Approved by Chairman May 1, 1942

ACKNOWLEDGMENTS

On the completion of this work, the author wishes to express his sincere gratitude to Dr. Wyatt C. Whitley not only for his suggestion of this problem but also for his helpful assistance and guidance. The author also wishes to thank Mr. Holly, Chief Chemist of the State Experiment Station, Experiment, Georgia, for his cooperation and interest in this problem.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PURPOSE

The amount of zinc present in soybeans is of great importance today; especially in Georgia, where soybeans have become a major commodity. Agriculturalists of the State are interested in finding out the composition of soybean ash in order to know what variety of soybean is best adapted to this locality. Therefore it is the purpose of this study to determine zinc, quantitatively and qualitatively, in certain varieties of soybeans. With this objective in view, three varieties of soybeans, recommended and furnished by the State Experiment Station at Experiment, Georgia, were obtained. Since these beans were grown on the same type of soil and under the same condition, comparison as to their zinc content could be made.

FOREWARD

The importance of zinc in plant nutrition has received considerable attention in recent years, and this has led to the investigation of methods of determination of zinc in plant materials and in soils. The most promising has been the colorimetric method suggested by Lott[1], the dithizone separation as used by Hibbard[2], spectrographic methods as outlined by Rogers and Gall[3], and polarographic methods. Lott's colorimetric method involves a hydrogen sulfide precipitation and complete separation of zinc from other constituents. The dithizone separation is acknowledged to be neither as precise nor as easy to carry out as the spectrographic or dropping mercury electrode method[4]. The apparatus required for quantitative measurements by means of the dropping mercury electrode is less expensive than the spectrographic method, and the method is comparatively simple in the case of zinc in plant materials and soils.

---

[1] Lott, W. L., Ind. Eng. Chem., Anal. Ed., 10, 335 (1938)

[2] Hibbard, B. L., Ibid., 10, 615 (1938)

[3] Rogers, L. A., and Gall, O. E., Ibid., 9, 42 (1937)

[4] Hibbard, B. L., Ibid., 9, (1937)

THE POLAROGRAPHIC ANALYSIS OF ZINC IN THREE VARIETIES OF SOYBEANS

INTRODUCTION

The polarographic method of chemical analysis was introduced about twenty years ago by Professor Jaroslav Heyrovsky,[1] and its development up to the present time is due in large part to the efforts of this investigator and his colleagues. The method is based on the interpretation of the current-voltage curves that are obtained when solutions of electroreducible or electrooxidizable substances are electrolyzed in a cell in which one electrode consists of mercury falling dropwise from a very fine bore capillary glass tube. From the unique characteristics of such current-voltage curves, both the species and the concentration of the electroreducible or electrooxidizable substances present in the solution can be determined.

In 1925 Heyrovsky and Shikata[2] invented an instrument called the polarograph, with which dropping electrode current-voltage curves are obtained automatically. The recorded curves are called polarograms.

---

[1] Kolthoff, I. M., and Lingane, J. J., Polarography, Inter-science Publishers, Inc., New York, New York City, page 3, (1941)

[2] Heyrovsky, J., and Shikata, M., Rec. Trav. Chim., **44**, 496 (1925)

In certain favorable cases, it is possible to simultaneously detect and determine as many as five or six different substances from a single polarogram. The method is especially suitable for small concentrations (10^{-2} to 10^{-6} molar), and since the analysis can be performed with a very small volume of solution, mere traces of substances can be determined. A wide variety of organic substances, as well as most of the common reducible inorganic ions, can be determined. These facts, coupled with the advantage that a simultaneous qualitative and quantitative analysis is obtained in a single operation, make the polarographic method a valuable new addition to present analytical methods.

The type of dropping electrode that is now commonly employed in polarographic analysis was originally designed by Professor G. Kucera at the Charles University in Prague some forty years ago for a quite different purpose, namely, for investigations of the electrocapillary curve of mercury in various electrolyte solutions.[3] During the course of his investigations Kucera observed certain peculiar inflections in the electrocapillary curve when the solution contained reducible substances. Thus at the suggestion of Professor Kucera and for the purpose of further studying these "anomalies", Heyrovsky began his investigations with

---

[3]Kucera, G., Ann. Physik, 11, 529 (1903)

the dropping electrode that ultimately led to the development of the polarographic method of analysis.

In this country, I. M. Kolthoff at the University of Minnesota and J. J. Lingane[4] at the University of California have made outstanding contributions to the field of polarography, while O. H. Muller[5] of Cornell University has also done a great deal of work with organic compounds.

---

[4] Kolthoff, I. M., and Lingane, J. J., Chem. Rev. 24, 1-94 (1939)

[5] Muller, O. H., Chem. Rev. 24, 95-124 (1939)

THEORETICAL DISCUSSION

REDUCTION POTENTIAL

A reversible reduction reaction at the dropping mercury cathode involves an exact quantitative change of free energy such that, for ion (A^+),

$$A^+ + e = A + \Delta F \qquad (1)$$

in which (ΔF) is a characteristic quantity per equivalent of chemical change and is in turn expressible by the relation,

$$\Delta F = -96{,}494\ n\ E \qquad (2)$$

Thus, the reduction potential (E) is characteristic of the reducible substance. To carry out this reduction reaction, free energy must be supplied to the system by an impressed voltage and therefore the value of the impressed voltage corresponding with the initiation of the electrode reaction can be made a quantitative test for the substance being reduced. If, by reduction potential, reference is made to a tangent potential or any other equivalent measure of initial discharge, then such a reduction potential varies with the concentration of the reducible substance with the usual relations,

$$E = E_o - \frac{RT}{nF} \ln \frac{a_{Red}}{a_{Ox}} \qquad (3)$$

Where R is the gas constant, T is the absolute temperature, n is the number of electrons involved in the reaction, F the Faraday, and ^{a}Red and ^{a}Ox the activities of the reductant and oxidant, respectively. E_o is the electrode potential characterizing the oxidation-reduction system when the activities of the oxidant and reductant are equal. To make this equation applicable to an electrode during electrolysis we have to use the activities of the reactants as they exist at the electrode surface and not those existing in the body of the solution. For convenience we shall use the following less accurate form of equation (3),

$$E = E_o - \frac{RT}{nF} \ln \frac{[Red]_i}{[Ox]_i} \quad (4)$$

where the brackets indicate concentrations instead of activities and the subscripts i denote that we deal with the concentrations at the electrode-solution interface only.

The reduction tangent potential for a given reducible ion thus becomes more positive the greater the concentration of that ion and, in the case of a monovalent ion electrolized at 25°C, multiplication of the concentration by the factor 10 displaces the reduction potential 59 millivolts to the left of the polarogram. This relation may be used as a test for the reversibility of a proposed electroreduction position.

HALF WAVE POTENTIAL

While the tangent potential is dependent upon the concentration of the reducible or oxidizable substance, the drop time of the electrode and the galvanometer sensitivity, the half wave potential is invariable and can be used as an identifying property. It has been shown by Heyrovsky and Ilkovic[1] that the inflection point of a polarographic current step occurs at a potential corresponding with one-half the diffusion current value or one-half the full height of the step; this inflection potential is called the half wave potential.

When the cathodic current, i.e., the current observed during a reduction, is governed only by the rate of diffusion of the oxidant, it is a function of the difference in concentration between the depleted inter-surface and the body of the solution and can be expressed as follows:

$$I = K \left([Ox] - [Ox]_i \right) \qquad (5)$$

Where I is the current and [Ox] is the concentration in the body of the solution, while $[Ox]_i$ has decreased to a value which is negligibly small compared to the metal ions in the body of the solution. In other words, at potentials corresponding to the diffusion current, the metal ions are reduced as rapidly as they diffuse up to the electrode surface. Therefore $[Ox]_i$ in equation (5) can be neglected and

---

[1] Ilkovic, D., Collection Czechoslov Chem. Commun., 7, 198 (1935)

$$I_d = K\ [Ox] \qquad (6)$$

by combining equations (5) and (6), the following expression is obtained

$$[Ox]_i = (I_d - I) / K \qquad (7)$$

The concentration of the reaction product at the interface $[Red]_i$ must be proportional to the current I, so that

$$[Red]_i = kI \qquad (8)$$

where k is again a diffusion constant.

We can now substitute equation (7) and (8) into equation (4) to get

$$E = E_o - \frac{RT}{nF} \ln \frac{kIK}{I_d - I} \qquad (9)$$

or

$$E = E_o - \frac{RT}{nF} \ln \frac{I}{I_d - I} - K' \qquad (10)$$

In the case of the half wave potential, I is equal to $(I_d - I)$ by definition, so that the logarithmic term drops out:

$$E_{\frac{1}{2}} = E_o - K' \qquad (11)$$

This means that the half wave potential of the dropping mercury electrode is equal to the normal electrode potential of the reacting system minus some constant.

According to Heyrovsky and Ilkovic[2] this constant is a function of the diffusion coefficients of the oxidant (D_{Ox}) and reductant (D_{Red}) as given by the following equation:

$$K' = \frac{RT}{2nF} \ln \frac{D_{Ox}}{D_{Red}} \qquad (12)$$

The ratio of the diffusion coefficients is assumed to be close to unity so that K′can usually be neglected.

Though equation (11) can be applied to reversible reactions involving electrodeposition, it is equally applicable to reversible electroreduction processes for simple ions. But when either electrodeposition or electroreduction is carried out with the reducible cation in the nature of a complex ion, the half wave potential is shifted by an amount representing the free energy of the complex ion formed in the reaction. Thus the half wave potentials may change with changing pH of the electrolyte, as in the case of amphoteric elements.

RELATION OF CATHODE POTENTIAL AND POLAROGRAPHIC VOLTAGE

The voltage (E) applied to the cell by the polarograph is evidently disturbed in three parts as follows:

$$E = E_C + E_A + IR \qquad (13)$$

---

[2] Heyrovsky, J., and Ilkovic, D., Collection Czechoslov. Chem. Commun., 7, 198 (1935)

Where E_C and E_A are the cathode and anode potentials respectively, I the current and R the resistance.

The factor (IR) is made negligible in polarographic practice by maintaining a low internal resistance, assured by the presence of a strong electrolyte in a relatively great concentration.

Then, within practical limits of measurement, when the dropping electrode is cathodic, the true cathode potential differs from the polarographic voltage only by the value of the anode potential. Since the anode potential is a variable quantity depending on the nature and concentration of the foreign salts present in the solution, the values of the half wave applied E. M. F. are not characteristic of the reducible substances present. However, if the anode potential is known, the characteristic half wave potentials of the dropping electrode can be easily found from the applied voltage when this is also known.

The usual practice is to measure the anode potential against an external calomel reference electrode, either at the beginning or at the end of the experiment, and the potential of the dropping electrode is then computed from the simple relation,

$$E = E_C - E_A \qquad (14)$$

In this equation, E is the total E. M. F. applied to the cell, E_C is the half wave potential of the dropping electrode, and E_A is the value of the saturated calomel electrode-pool potential.

CURRENT MEASUREMENT

The height of a current step which begins as a function of the local concentration of a discharging ion is limited by the rate at which this ion is supplied to the electrode by: (1) a diffusive force, proportional to the concentration gradient between the surface of the mercury drops and the body of the solution, and (2) an electrical force, proportional to the electrical potential gradient around the mercury drops. In general, then, reducible ions are supplied to the surface of the dropping electrode partly by diffusion and partly by electrical migration, so that the limiting current may be regarded as the sum of a "diffusion current" and a "migration current."

The current through an electrolyte solution is carried impartially by all the ions present. The fraction of the total current carried by any particular species of ion depends on its relative concentration in the solution, and, to a lesser degree, on its valence and intrinsic mobility; in other words, on its transference number in the particular solution in question. Therefore, if a large excess of an

indifferent salt[3] is added to a solution of a reducible salt, the current through the solution will be carried practically entirely by the ions of the added salt. Under these conditions electrical migration of the reducible ions, and hence the migration component of the limiting current, will be practically completely eliminated, and the limiting current will be solely a diffusion current.

Ilkovic[4] has established that the diffusion current, or step height (i), is related to concentration (c), diffusion coefficient (D), mass of mercury (m) discharged per second from the cathode, and time in seconds (t) per drop of mercury in the following manner,

$$i = 0.63 \cdot nf \cdot c \cdot D^{\frac{1}{2}} \cdot m^{\frac{2}{3}} \cdot t^{\frac{1}{6}} \qquad (15)$$

from which it follows that in the reduction of a specific ion at a specific cathode with constant discharge and dropping rates.

$$i \propto C \qquad (16)$$

---

[3] An indifferent salt, in electroreductions, is one that is reduced at a more negative potential than the reducible substance in question, and one that does not form complexes, or react specifically in other ways, with the reducible substance. Because of their very negative reduction potentials, the salts of the alkalies, alkaline earths, and ammonium salts are usually used as indifferent salts. Tetrasubstituted alkyl-ammonium salts are commonly used also as indifferent salts in polarographic analysis of the alkali and alkaline-earth ions.

[4] Ilkovic, D., Collection Czechoslov., Chem. Commun., 7, 198 (1935)

STANDARDIZATION OF CELL

For exact duplication of the current concentration ratio, the factors whose control is necessary, as well as the degree in which each affects that ratio, are shown by equation (15). Varying each factor singly, others being held constant, it is evident that

$$\begin{aligned} i &\propto D^{\frac{1}{2}} \\ i &\propto m^{\frac{2}{3}} \\ i &\propto t^{\frac{1}{6}} \end{aligned} \qquad (17)$$

The diffusion constant (D) is dependent upon the frictional resistance (F) of the solution thus according to Fick's First Law.[5]

$$D = \frac{RT}{nF} \qquad (18)$$

where n is the number of electrons involved in the reduction of one molecule of the reducible substance, F is the Faraday, R is the gas constant and T the absolute temperature; and so is affected by changes in the viscosity of the solution. But since the current is proportional to the square root of the diffusion constant, the viscosity of ordinary solutions is sufficiently controlled by the assurance of roughly similar electrolyte content.

---

[5] Fick, A., Pogg. Ann. 94, 59 (1855)

More critical in its effect is the mass of mercury (m) discharged per second from the capillary, since this factor appears in its two-thirds power. It has beenshown[6], however, that (m) is proportional to the height of the mercury reservoir (h) and to the capillary orifice, other capillary characteristics being constant; and that, using a given capillary

$$i \propto h^{\frac{1}{2}} \qquad (19)$$

This means that for duplicate analyses using the same capillary, (m) is sufficiently well reproduced by approximate constancy of the position of the mercury reservoir.

As a working guide, the temperature should be controlled to at least 0.5°C., or better, in order to keep errors due to the temperature effect within 0.1 per cent. Thus for greatest accuracy, either thermostat control is employed or exact temperature measurements made and standardization curves corrected accordingly.

---

[6] Kolthoff, I. M., and Lingane, J. J., Chem. Rev., 24, 1 (1939)

APPARATUS AND MATERIALS

The most important piece of apparatus used in this problem was a Fischer Elecdropode. It is an instrument for conducting chemical analysis by means of the dropping mercury electrode which has been designed to take full advantage of the very recent advances in this technique. The basic principles remain the same as those established by Heyrovsky and his co-workers.

The Fischer Elecdropode is a self-contained unit which is compact and portable and may be used in any place where alternating current is available for operating the galvanometer lamp. The operating potential is supplied by a set of dry cells contained in the case and these cells are standardized just before use against an Eppley Standard cell. On the panel, or the front of the case, are all the controls and brackets necessary for operation, including a holder for the beaker in which the test solution is placed. When in position on the holder, the beaker is so held that the dropping electrode, the contact with the mercury pool on the bottom of the beaker, a saturated calomel electrode and a stopcock for flushing the solution with hydrogen are all held in proper position.

From a long galvanometer scale, the current is read as the potential applied to the electrode is increased. In actual use, it is quite possible to do quantitative work by making current readings over a voltage range as small as 0.1

of a volt. During the analysis, the sensitivity may be varied from 1 to $\frac{1}{500}$ in order to obtain the best current-voltage curves. An advantage of this system lies in the fact that the actual current values are recorded as read and it is not necessary subsequently to determine them by measurement from a recorded curve.

It may be noted, however, that no provision is made for themostating the electrolysis cell, which should be done in accurate work because the diffusion current varies considerably with temperature. This difficulty, however, can be avoided by heating the solution to be tested in a constant temperature bath.

MATERIALS

A brief description of the varieties of soybeans used in this problem are as follows:

(a) Doxi. A natural hybrid found in the Doxi variety. Medium late in maturing, about October 25. Not in commercial production but appears very promising from the grain standpoint. Medium sized yellow seed.

(b) Rokusun. An early maturing edible type bean very poor yielder and shatters readily. Grown because of its good edible quality either green or dry. It is a large yellow bean and its skin has a tendency to crack.

(c) Laredo. An early hay type variety. Matures about October 10. Has been grown in Georgia for many years. A reliable yielder grown mainly because of its early maturity. They are small black seeds.

Solutions used[1]:

1. Methyl Red--0.2% alcoholic solution
2. Bromo-cresol green--0.2% alcoholic solution
3. Potassium chloride--exactly 1N solution
4. Hydrochloric acid--concentrated solution, approximately 12 N
5. Hydrochloric acid--dilute solution, approximately 1N
6. Zinc chloride--approximately a 2×10^{-2} N solution
7. Potassium permanganate--a saturated solution
8. Sodium hydroxide--approximately 6 N solution

The mercury used was U. S. P. Redistilled. After about twenty analyses the mercury was treated with mercuous nitrate, washed with water and dried[2]. This proved to be a very rapid method of cleaning mercury.

---

[1] All the chemicals used were C. P. unless otherwise stated. Distilled water was also used in preparing these solutions.

[2] Easly, H. F., Ind. Eng. Chem., Anal. Ed., 9, 82 (1937)

PROCEDURE

A 45 to 75 gram sample of the soybeans was ashed in a muffle furnace below 450°C. because above this temperature zinc oxide has an appreciable vapor pressure. At this point the ash was usually white or slightly yellow[1]. The ash was placed in a desiccator and finally weighed. Then the ash was treated with 50 cc of concentrated hydrochloric acid, placed in a 200 cc beaker, and evaporated to dryness; this was done in order to concentrate the sample. The residue obtained was treated with 25-35 cc of approximately 0. 1N hydrochloric acid. Next, the solution was heated on a hot plate for several minutes and then filtered. A black residue was usually obtained, but upon ignition it was found to contain only carbon.

To the filtrate, 10 cc of 1N potassium chloride was added and the filtrate was finally diluted to 100 cc so that the final concentration of the potassium chloride was 0.1N. In case the filtrate was diluted to 250 cc, the 25 cc of 1N potassium chloride was added.

In the following analysis, a 50 cc-portion was always used. Before any current voltage readings were taken, it was necessary to add 15 drops of methyl red

---

[1] If the residue was black, the ash was ignited for several more hours.

and 10 drops of bromo-cresol green to the sample for the purpose of suppressing a maximum[2]. Before the analysis was started, hydrogen was passed through the solution for fifteen minutes; but during the analysis, hydrogen was passed over the solution in order to prevent any oxygen from redissolving in the solution.

The current-voltage readings were taken with the same capillary, the mercury reservoir in the same position, and the temperature maintained between 28.5° and 29°C. According to Ilkovic's diffusion current equation, all these factors have to remain constant in order for the height to be proportional to the concentration. The two best sensitivities used were $\frac{1}{20}$ and $\frac{1}{50}$.

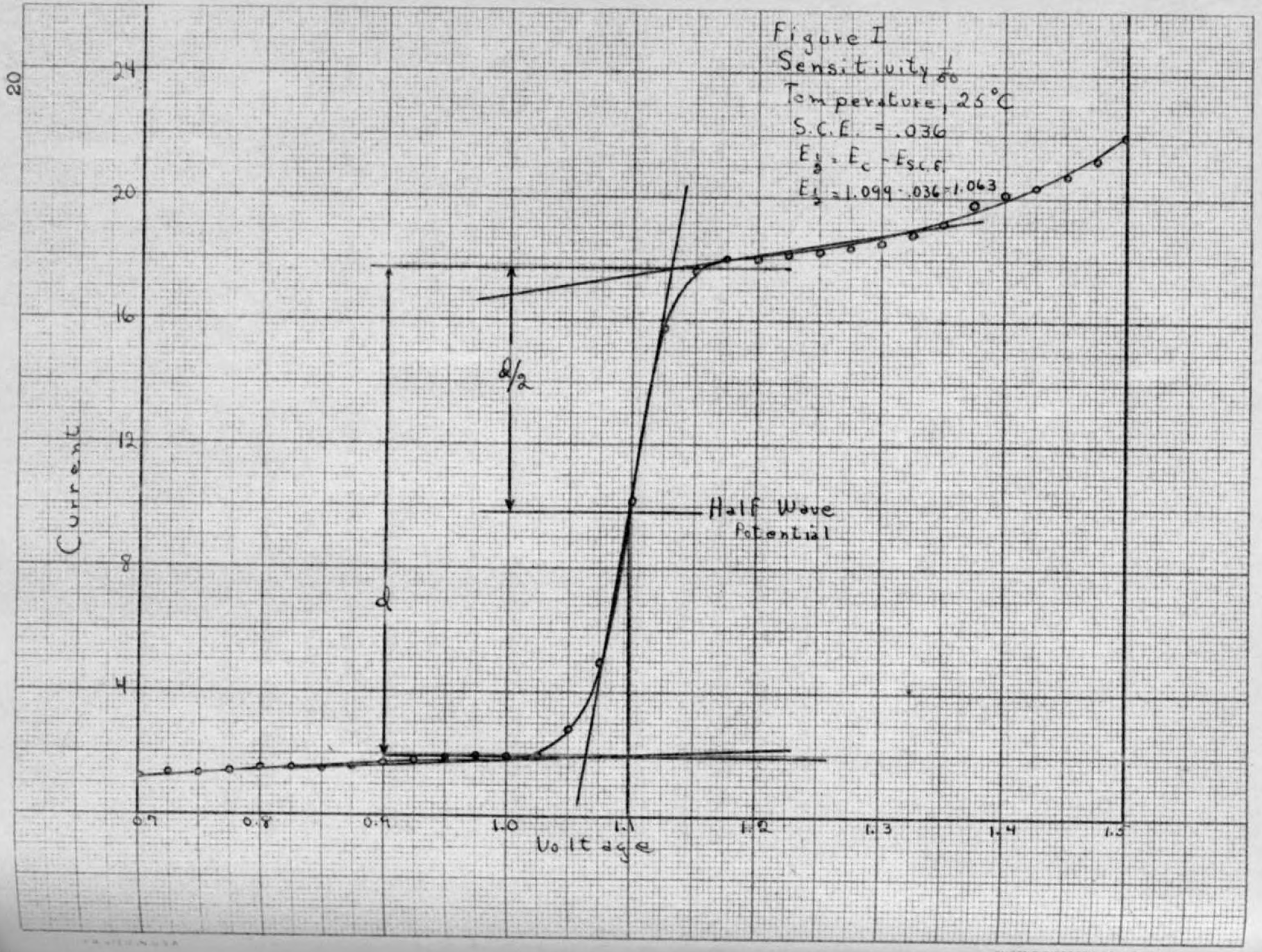
---

[2] It happens occasionally that the current voltage curves, instead of appearing as a series of plateaus, will show a pronounced peak at which would normally be the top of the current rise. This occurs in certain types of electrolytes containing a reducible ion which is more or less strongly on the surface of mercury cathode. However, the height of this maximum can be suppressed by the addition of a second substance which is likewise absorbable but not reducible at the voltage value of the maximum.

METHOD OF CALCULATION

For quantitative analyses which are to be repeated frequently, it is necessary to prepare a standard curve by the preparation of test solutions similar in non-reducible composition to that expected to be found in subsequent analyses. The test solutions used differed only with respect to known concentrations of the component to be measured. These data, plotted against millimeters of current step height must be determined at the same temperature at which tests will be made regularly and must be established by a number of points in the same order of magnitude as that anticipated for the concentration of the unknown. All the standardization tests were made with the same capillary and the same reservoir elevation. Any standardization must, of course, specify the sensitivity ratio with which it was derived. However, the concentration value at the sensitivity ratio of the calibration may be converted to an equivalent value at another sensitivity ratio simply by applying the ratio factor of the first sensitivity to the second.

Many different methods are used for measuring the current step height, the important rule being, however, that comparative curves must be measured by the same method. The method most generally applicable and the one used in this study is the intersection method illustrated in Figure (I).



It is carried out in the following steps:

(1) With the straight edge, lay on the curve straight line extensions of the principal slopes of the curve before and after the current step, placing these slope lines through the most representative portion of the slope;

(2) Similarly, draw a slope line through the principal rising section or the step;

(3) Draw through the points or intersections of the three slope lines, lines parallel with the voltage axis. The step height is then the vertical distance between the two parallels.

The half wave potential is then determined by drawing a line parallel to the horizontal axis at a distance of one-half the step height. At the point where this line meets the rising section of the step, a line is dropped perpendicularly until it meets the voltage axis. The correct half wave potential is then found by use of the equation:

$$E = E_c + E_A \qquad (14)$$

$$E_c = E - E_A \qquad (20)$$

where E_c is the half wave potential, E is the voltage applied to the cell and E_A the saturated calomel electrode-pool potential.

EXPERIMENTAL DATA

Before proceeding with the polarographic analysis of different varieties of soybeans, a spectrographic analysis was made of the Doxi variety of soybean. This preliminary step was taken in order to determine the main constituents of soybeans and their relative concentrations. The spectrograph showed that soybean ash contained chiefly the following elements: phosphorus, magnesium, manganese, aluminum, copper, iron, boron, sodium, potassium, and calcium. It was interesting to note that the spectrographic analysis gave no indication of zinc being present in the soybean ash.

QUANTITATIVE STANDARDIZATION

For quantitative analyses which are to be repeated frequently, it is necessary to prepare a standard curve by the preparation of test solutions similar in non-reducible composition to those expected to be found in subsequent analysis. Thus, a stock solution of approximately 0.01 M zinc chloride was made and five solutions of different concentrations were made from the stock solution. Each of the five zinc chloride solutions was measured accurately in a volumetric flask. In order to know the exact concentration of these five solutions, the stock solution was analyzed quantitatively by a gravimetric method, and the concentrations

of the solutions calculated from this datum. The procedure was as follows:[1]

> Two samples of 250 cc each were made alkaline with ammonium hydroxide and then buffered with ammonium chloride. Dilute hydrochloric acid was added until the reaction was faintly acid. Then 15 cc of 50 per cent ammonium acetate was added and finally hydrogen sulfide was passed into the solution for a few minutes until precipitation was complete. The precipitate was allowed to settle and the zinc sulfide separated by filtration. The zinc sulfide was placed in a previously-weighed crucible and ignited at a bright red heat. The cruciblesswere then cooled and the weight of zinc oxide was found. The weight of Sample A was 0.2111 g and the weight of Sample B was 0.2109 g, or the average weight of zinc oxide was 0.2110 g. From this weight of zinc oxide, the exact normality of the stock solution was found to be 0.0207 N, or 0.0104 M.

The five zinc chloride solutions mentioned previously were analyzed polarographically and the height of each current step was measured; the results are recorded in Table I. These data plotted as concentration against millimeters of step height were determined at the same temperature, with the same capillary and the same mercury reservoir elevation as used in the analysis of the soybean ash. Figures II and III show the standardization curves for zinc at a sensitivity of 1/20 and 1/50.

---

[1] Griffin, R. C., Technical Methods of Analysis, McGraw-Hill Company, New York City, Page 529 (1927).

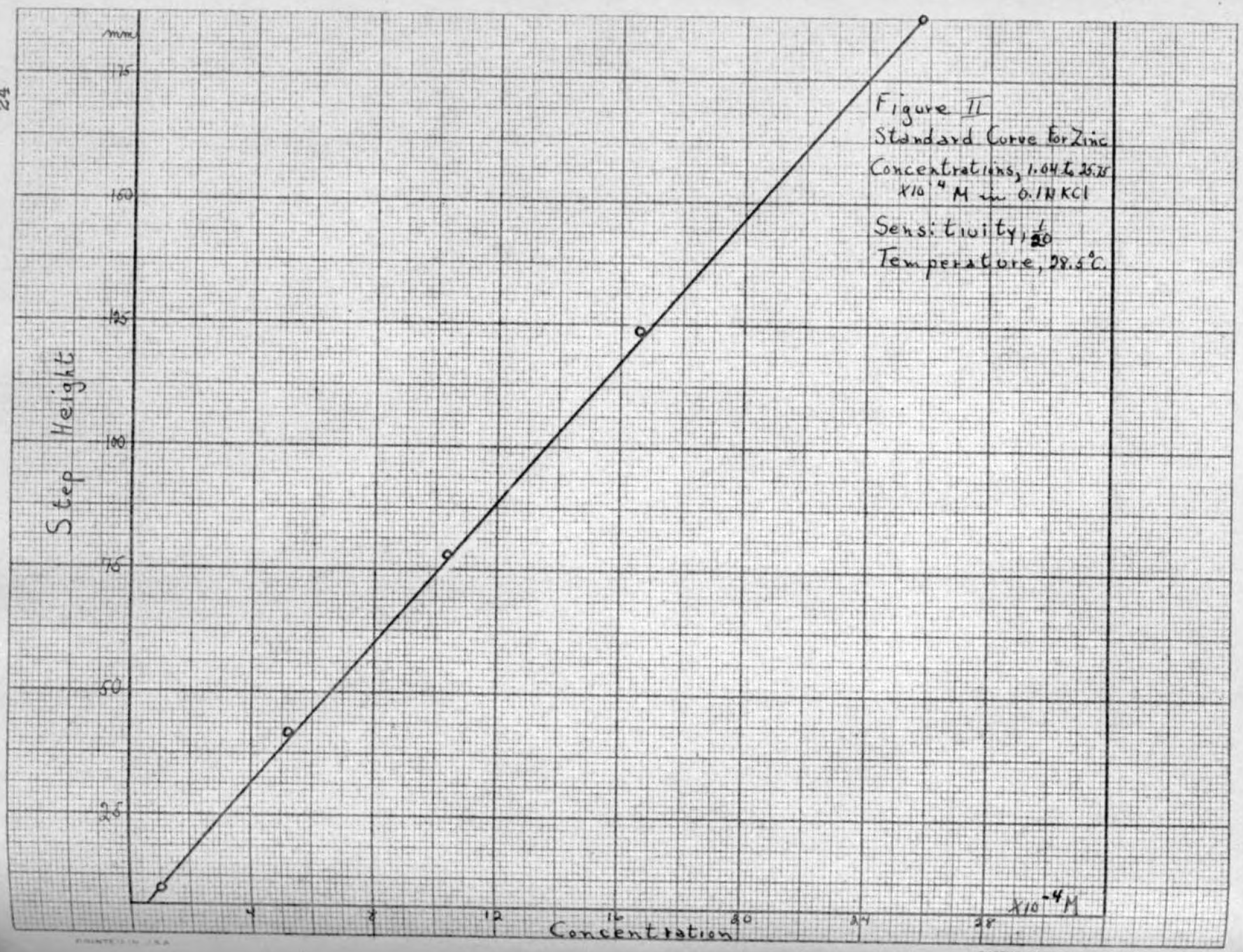


Figure II
Standard Curve for Zinc
Concentrations, 1.04 to 25.35 X10⁻⁴ M in 0.1N KCl
Sensitivity, 1/20
Temperature, 28.5°C.

Figure III
Standard Curve for Zinc
Concentrations, 1.04 to 25.25 x 10^{-4} M
in 0.1 KCl
Sensitivity, 1/50
Temperature, 28.5°C

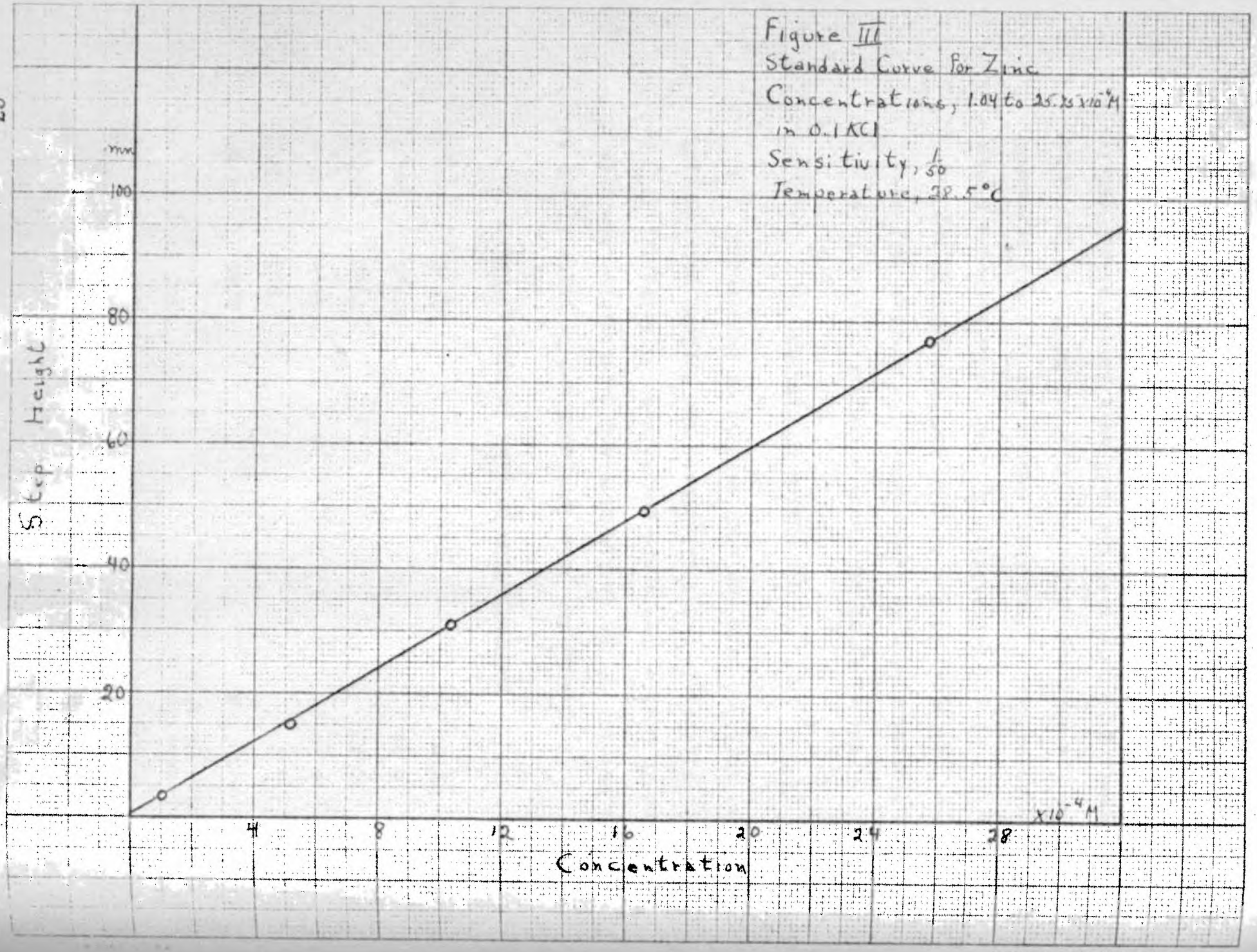


TABLE I

Concentration of Zinc Chloride	Step Heightin mm. Sensitivity	
x 10^{-4} M	1/20	1/50
1.04	9.8	3.5
5.19	41.8	15.0
10.37	79.8	31.1
16.59	124.0	49.7
25.75	187.8	77.2

DETERMINATION OF ZINC IN DOXI SOYBEANS

Following the procedure outlined on pages 17 and 18, the results of the qualitative and quantitative analysis of zinc in Doxi soybeans are summarized in Tables II, III, and IV. Figures IV and V illustrate the typical polarographic wave obtained from the Doxi variety of soybean.

DISCUSSION OF RESULTS

The accepted half wave potential of zinc in an acid or neutral medium is 1.06 volts. The average half wave potential obtained for zinc in the Doxi variety was 1.054 volts, using a sensitivity of 1/20 and 1.065 using a sensitivity of 1/50. Thus these values are in close agreement with the accepted half wave potential of zinc. It was interesting to note that the half wave values with a sensi-

TABLE II

QUALITATIVE DETERMINATION OF ZINC IN DOXI VARIETY

Sample Number	Half Wave Potential of Zinc in Volts	
	Sensitivity 1/20	Sensitivity 1/50
1	1.0680	1.0710
2	1.0520	1.0580
3	1.0608	1.0698
5	1.0660	1.0760
9	1.0562	1.0602
10	1.0580	1.0580
11	1.0560	1.0680
12	1.0540	1.0540
13	1.0697	1.0737
14	1.0600	1.0970
15	1.0596	1.0786
16	1.0585	1.0700
17	1.0379	1.0429
18	1.0400	1.0490
19	1.0370	1.0570
20	1.0350	1.0510
Average:	1.0536	1.0648

TABLE III

QUANTITATIVE DETERMINATION OF ZINC IN DOXI VARIETY

Sensitivity of 1/20

Sample Numoer	Weight in Grams Sample	Ash	Step Ht. in mm.	Molarity of Sample x 10^{-4}M	Per Cent of Zinc Sample	Ash
*1	69.5573	3.1463	35.9	4.65	0.0102	0.232
*2	76.0432	3.4546	35.0	4.50	0.0089	0.195
3	69.2228	3.1452	33.8	4.35	0.0086	0.189
**5	114.2143	5.4039	29.5	3.75	0.0112	0.236
9	55.9118	2.5109	31.0	3.93	0.0096	0.214
10	45.3672	2.0483	25.5	3.20	0.0096	0.213
11	50.7990	2.2990	26.5	3.35	0.0090	0.199
12	52.5336	2.3816	31.1	3.95	0.0102	0.228
**13	50.4967	2.3814	15.1	1.75	0.0118	0.250
**14	55.3859	2.6261	15.9	1.92	0.0118	0.259
**15	50.8382	2.3598	14.8	1.70	0.0114	0.245
**16	50.4026	2.3634	12.8	1.50	0.0101	0.217
17	50.2979	2.3022	26.7	3.40	0.0092	0.202
18	51.3231	2.3332	26.5	3.35	0.0089	0.198
19	48.6192	2.2713	25.0	3.12	0.0089	0.187
20	52.6148	2.4592	28.3	3.60	0.0093	0.200
Average:					0.0099	0.216

* Sample was diluted to 110 cc instead of 100 cc.

** Sample was diluted to 250 cc instead of 100 cc.

TABLE IV

QUANTITATIVE DETERMINATION OF ZINC IN DOXI VARIETY

Sensitivity of 1/50

Sample Number	Weight in Grams Sample	Ash	Step Ht. in mm.	Molarity of Sample x 10^{-4}M	Per Cent of Zinc Sample	Ash
*1	69.5573	3.1463	13.20	4.50	0.0097	0.215
*2	76.0432	3.4546	14.00	4.75	0.0094	0.206
3	69.2288	3.1452	13.90	4.70	0.0093	0.204
**5	114.2143	5.4039	12.70	4.35	0.0130	0.275
9	55.9118	2.5109	10.80	3.70	0.0090	0.201
10	45.3672	2.0483	7.90	2.70	0.0081	0.180
11	50.7990	2.2990	11.80	4.00	0.0107	0.237
12	52.5336	2.3616	10.00	3.65	0.0095	0.211
**13	50.4967	2.3814	5.90	2.10	0.0142	0.300
**14	55.3859	2.6216	6.90	2.40	0.0148	0.311
**15	50.8382	2.3598	5.20	1.85	0.0124	0.267
**16	50.4026	2.3634	5.80	2.00	0.0135	0.289
17	50.2979	2.3022	12.90	4.40	0.0119	0.261
18	51.3231	2.3332	12.10	4.15	0.0110	0.243
19	48.6192	2.2713	11.90	4.05	0.0114	0.263
20	52.6148	2.4592	12.40	4.30	0.0111	0.239
Average:					0.0111	0.243

*Sample was diluted to 110 cc instead of 100 cc.

**Sample was diluted to 250 cc instead of 100 cc.

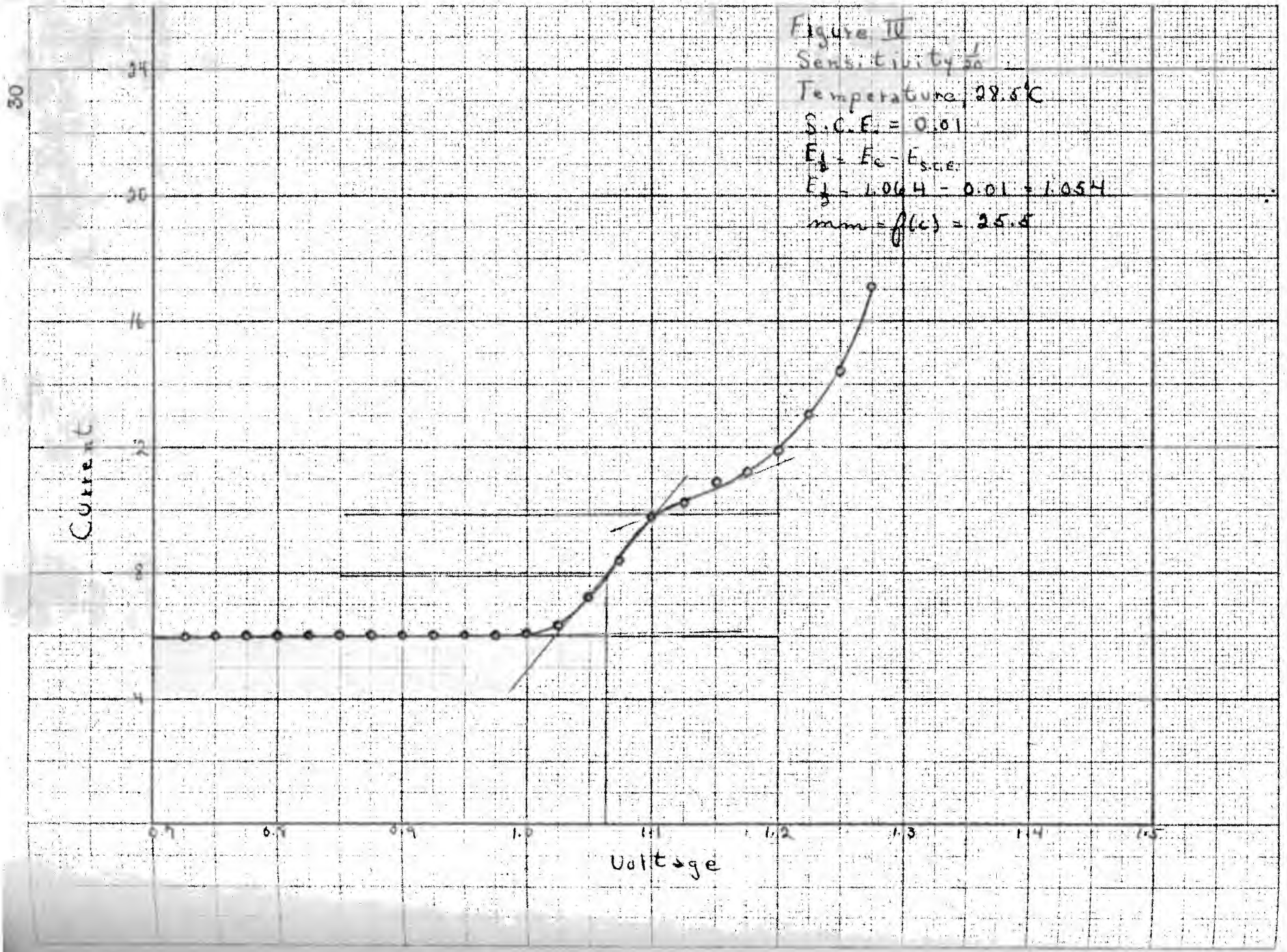


Figure IV
Sensitivity 1/20
Temperature 28.5°C
S.C.E. = 0.01
$E_b = E_c - E_{s.c.e.}$
$E_b = 1.064 - 0.01 = 1.054$
mm = f(c) = 25.5
Current
Voltage
24
20
16
12
8
4
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5

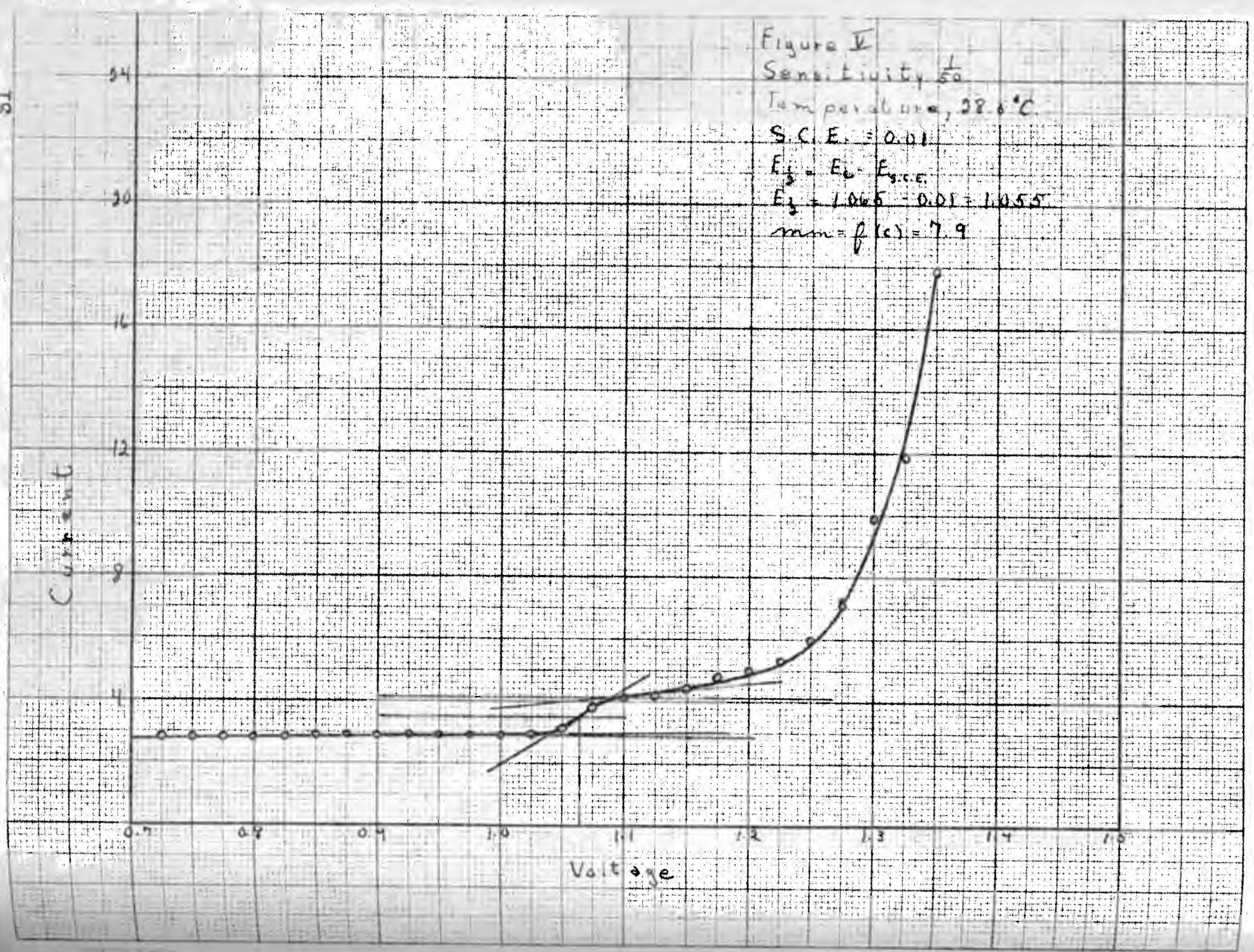


Figure V
Sensitivity $\frac{1}{50}$
Temperature, 28.6°C.
S.C.E. = 0.01
$E_{\frac{1}{2}} = E_{\frac{1}{2}} - E_{s.c.e.}$
$E_{\frac{1}{2}} = 1.065 - 0.01 = 1.055$
$mm = f(c) = 7.9$
Current
Voltage
24
20
16
12
8
4
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5

tivity of 1/20 were slightly smaller than the values obtained with a sensitivity of 1/50. This slight difference was probably due to the fact that the inherent error of the method was greater at the lower sensitivity.

In the quantitative determination of zinc in the Doxi variety of soybean, the average percentage of zinc was 0.0099 per cent when the sensitivity was 1/20. However, when a sensitivity of 1/50 was employed, the average percentage of zinc was 0.0111 per cent. Thus the average value in the second case was slightly higher than the average value obtained with a sensitivity of 1/20. This can be explained by two facts: (1) difficulty in reading the galvanometer scale and (2) the error involved in reading the step height in terms of molarity from the standardization curve.

By comparing the values obtained when a 100 cc sample was analyzed with those of a 250 cc sample, it was found that the percentages in the latter case were larger than those in the former. This would seem to indicate that the more dilute the solution, the larger the percentage of zinc. However, this was not the case, because the difference was due to the fact that the residue could not be as completely washed as it was in the case of the 250 cc sample.

The average percentage of zinc in the ash was 0.216 per cent when a sensitivity of 1/20 was used and 0.243 per

cent when 1/50 was the sensitivity. Again the values using the smaller sensitivity were higher than those found by the higher sensitivity. The large deviation in the values for the per cent of zinc in the ash can be explained by the fact that it was very difficult to weigh the ash accurately since it contained several hygroscopic salts like calcium chloride, magnesium chloride, and zinc chloride.

DETERMINATION OF ZINC IN ROKUSUN SOYBEANS

Adhering to the procedure previously outlined, the results of the qualitative and quantitative analysis of zinc in Rokusun soybeans are summarized in Tables V, VI, and VII. The zinc waves received from the polarographic analysis of Rokusun soybeans are given in Figures VI and VII.

DISCUSSION OF RESULTS

The average half wave potential found in zinc in the Rokusun variety of soybean using a sensitivity of 1/20 was 1.037 volts, and 1.043 volts with a sensitivity of 1/50. These values correspond closely to the accepted half wave potential of zinc in an acid or neutral medium 1.06 volts. As was the case of the Doxi variety, the half wave potentials obtained from the Rokusun variety were larger when a sensitivity of 1/50 was used.

TABLE V

QUALITATIVE DETERMINATION OF ZINC IN ROKUSUN VARIETY

Sample Number	Half Wave Potential of Zinc in Volts Sensitivity 1/20	Sensitivity 1/50
3	1.039	1.046
4	1.037	1.039
5	1.043	1.041
6	1.037	1.041
7	1.037	1.050
8	1.038	1.041
9	1.038	1.030
12	1.050	1.052
13	1.034	1.043
14	1.032	1.044
15	1.038	1.052
16	1.026	1.041
Average:	1.037	1.043

TABLE VI

QUANTITATIVE DETERMINATION OF ZINC IN ROKUSUN VARIETY

Sensitivity of 1/20

Sample Number	Weight in Grams Sample	Ash	Step Ht. in mm.	Molarity of Sample x 10^{-4}M	Per Cent of Zinc Sample	Ash
3	56.3308	2.8964	35.8	4.60	0.0111	0.216
4	50.6157	2.6057	32.1	4.15	0.0112	0.217
*5	65.1656	3.4563	18.6	2.25	0.0118	0.222
*6	66.6792	3.6954	18.8	2.30	0.0118	0.212
*7	58.4534	3.0328	17.8	2.10	0.0123	0.236
*8	52.1545	2.7330	13.4	1.55	0.0101	0.194
*9	51.1118	2.8222	16.2	1.95	0.0130	0.236
*10	58.7122	3.1633	18.1	2.15	0.0125	0.232
*11	52.4786	2.7580	17.0	2.03	0.0132	0.252
*12	47.3982	2.5795	14.9	1.72	0.0124	0.227
13	50.9931	2.6858	34.9	4.52	0.0121	0.229
14	43.8284	2.3612	25.9	3.25	0.0101	0.186
*15	54.9927	3.0003	15.8	1.90	0.0118	0.216
*16	53.0194	2.9254	13.8	1.60	0.0103	0.186
Average:					0.0117	0.219

*Sample was diluted to 250 cc instead of 100 cc.

TABLE VII

QUANTITATIVE DETERMINATION OF ZINC IN ROKUSUN VARIETY

Sensitivity of 1/50

Sample Number	Weight in Grams Sample	Ash	Step Ht. in mm.	Molarity of Sample x 10^{-4}M	Per Cent of Zinc Sample	Ash
3	56.3308	2.8964	15.2	5.35	0.0130	0.252
4	50.8157	2.6057	12.9	4.40	0.0118	0.230
*5	65.1656	3.4563	7.8	2.67	0.0140	0.264
*6	66.8732	3.6954	8.5	2.40	0.0120	0.221
*7	58.4534	3.0326	6.8	2.38	0.0139	0.268
*8	52.1545	2.7330	5.1	1.82	0.0119	0.227
*9	51.1118	2.6282	7.0	2.42	0.0161	0.293
*10	58.7122	3.1633	6.1	2.15	0.0135	0.232
*11	52.4786	2.7508	6.0	2.13	0.0138	0.264
*12	47.3982	2.5735	5.2	1.85	0.0113	0.245
13	50.9931	2.6858	14.8	4.95	0.0132	0.251
14	43.8284	2.3612	11.3	3.85	0.0120	0.232
*15	54.5927	3.0003	6.8	2.38	0.0148	0.268
*16	53.0154	2.9254	6.8	2.30	0.0148	0.268
Average:					0.0134	0.250

*Sample was diluted to 250 cc instead of 100 cc.

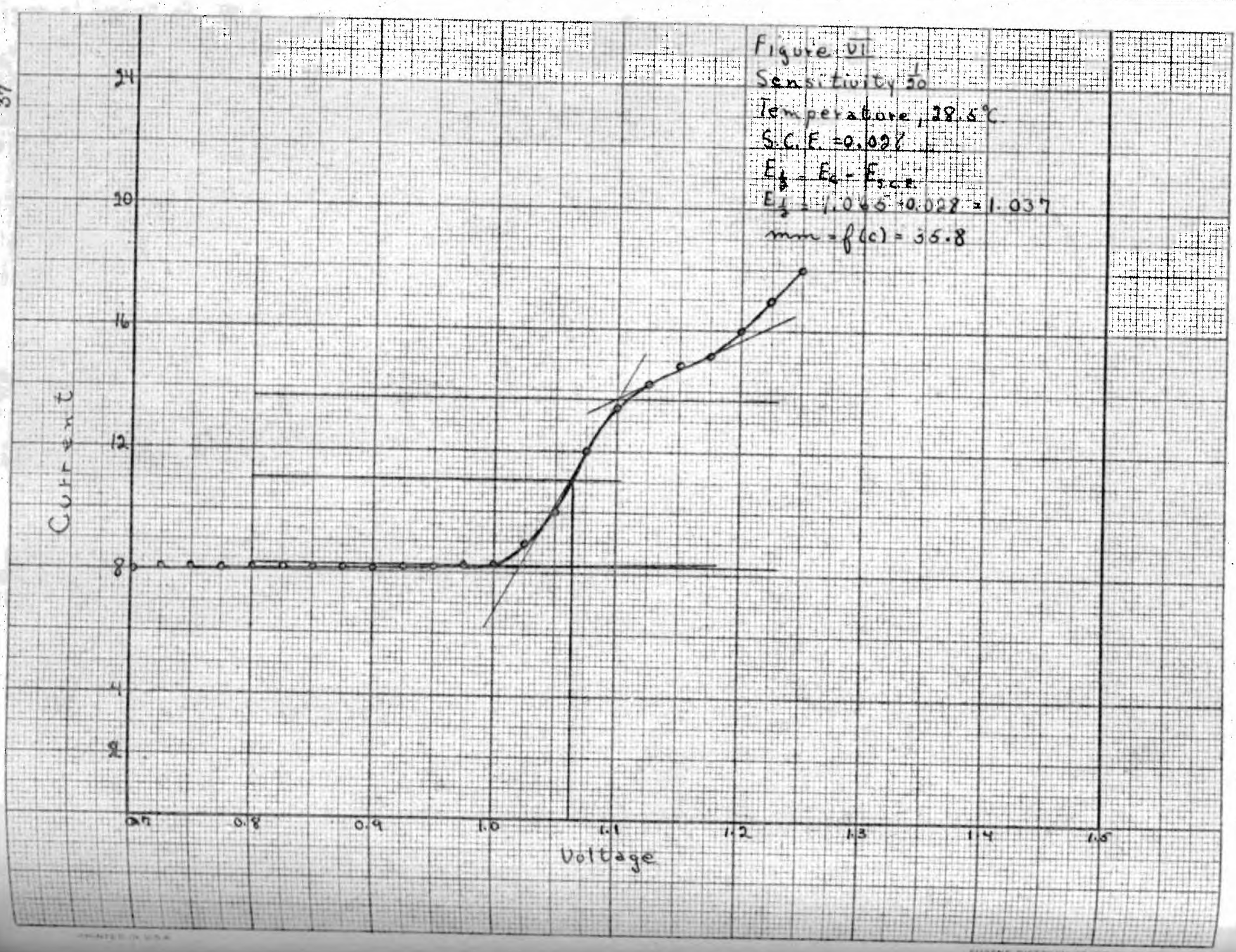
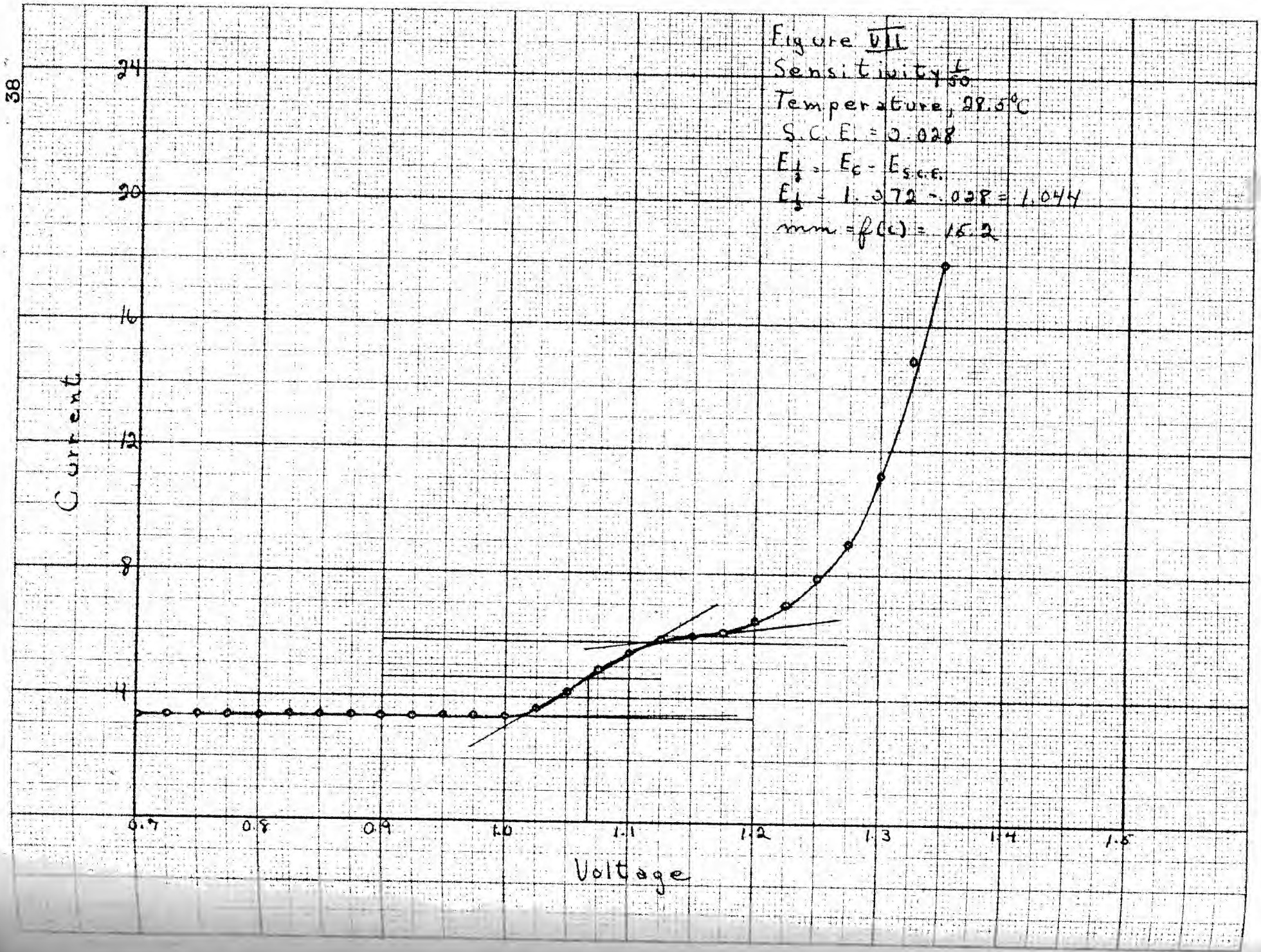


Figure VII
Sensitivity $\frac{1}{50}$
Temperature, 28.5°C
S.C.E. = 0.028
$E_{\frac{1}{2}} = E_c - E_{s.c.e.}$
$E_{\frac{1}{2}} = 1.072 - .028 = 1.044$
$mm = f(c) = 16.2$



The per cent of zinc in the Rokusun variety varied about the same as the percentage of zinc in the Doxi variety, When a sensitivity of 1/20 was employed, the average percentage was 0.0117, and when a sensitivity of 1/50 was employed, the average percentage was 0.0134. Again, the percentage of zinc was slightly higher when the smaller sensitivity was used. Also it should be noted that the 250 cc sample gave a higher percentage of zinc in the sample than the 100 cc sample.

In the determination of zinc in the ash, the average percentage was 0.219 per cent when a sensitivity of 1/20 or 1/50 were used respectively. The difference between these two percentages is greater than the difference between the percentage of zinc in the sample. This can be easily explained by the difficulty in weighing an ash which contains several hygroscopic salts.

DETERMINATION OF ZINC IN LAREDO SOYBEANS

Following the procedure outlined previously, the results of the qualitative and quantitative analysis of zinc in Laredo soybeans are given in Tables VIII, IX, and X. Typical zinc waves obtained by polarographic analysis of Laredo soybeans are given in Figures VIII and IX.

DISCUSSION OF RESULTS

For zinc in the Laredo variety of soybeans the average half wave potential was 1.010 when a sensitivity of 1/20 was used and 1.019 when a sensitivity of 1/50 was used. These values are slightly less than the accepted value of 1.06 but are within the limits of experimental error.

The percentage of zinc in the Laredo variety varied more than the percentage of zinc in the Rokusun and Doxi varieties. The average percentage with a sensitivity of 1/20 was 0.0107 per cent and 0.0113 per cent with a sensitivity of 1/50. As in the two previous varieties, the percentage of zinc was slightly higher when a sensitivity of 1/50 was employed.

In this variety, the percentage of zinc in a 100 cc sample was about the same as that in the 250 cc sample. Thus it can be concluded that the technique had been improved so as to insure complete washing of the ash residue, in spite of the small amount of wash liquid that was used.

The percentage of zinc in the ash was found to be 0.202 per cent with a sensitivity of 1/20 and 0.241 per cent with a sensitivity of 1/50. This agrees with the previous data because the percentage of zinc in the ash using a sensitivity of 1/50 was higher than that when a sensitivity of 1/20 was employed.

TABLE VIII

QUALITATIVE DETERMINATION OF ZINC IN LAREDO VARIETY

Sample Number	Half Wave Potential of Zinc in Volts	
	Sensitivity 1/20	Sensitivity 1/50
2	1.014	1.014
3	1.018	1.024
4	1.013	1.000
5	1.012	1.011
6	1.018	1.010
13	1.000	1.042
14	1.000	1.026
Average:	1.010	1.019

TABLE IX

QUANTITATIVE DETERMINATION OF ZINC IN LAREDO VARIETY

Sensitivity of 1/20

Sample Number	Weight in Grams Sample	Ash	Step Ht. in mm.	Molarity of Sample x 10^{-4}M	Per Cent of Zinc Sample	Ash
2	56.8462	2.9949	38.8	5.00	0.0120	0.227
**3	49.7978	2.6022	15.3	1.82	0.0125	0.239
**4	58.5556	3.0958	14.9	1.78	0.0104	0.196
5	41.1852	2.2163	24.0	3.02	0.0100	0.186
6	55.0438	2.9036	33.8	4.35	0.0108	0.204
*13	47.6608	2.4885	24.8	3.10	0.0098	0.187
14	48.8576	2.6289	26.4	3.35	0.0094	0.174
Average:					0.0107	0.202

*Sample was diluted to 110 cc instead of 100 cc.

**Sample was diluted to 250 cc instead of 100 cc.

TABLE X

QUANTITATIVE DETERMINATION OF ZINC IN LAREDO VARIETY

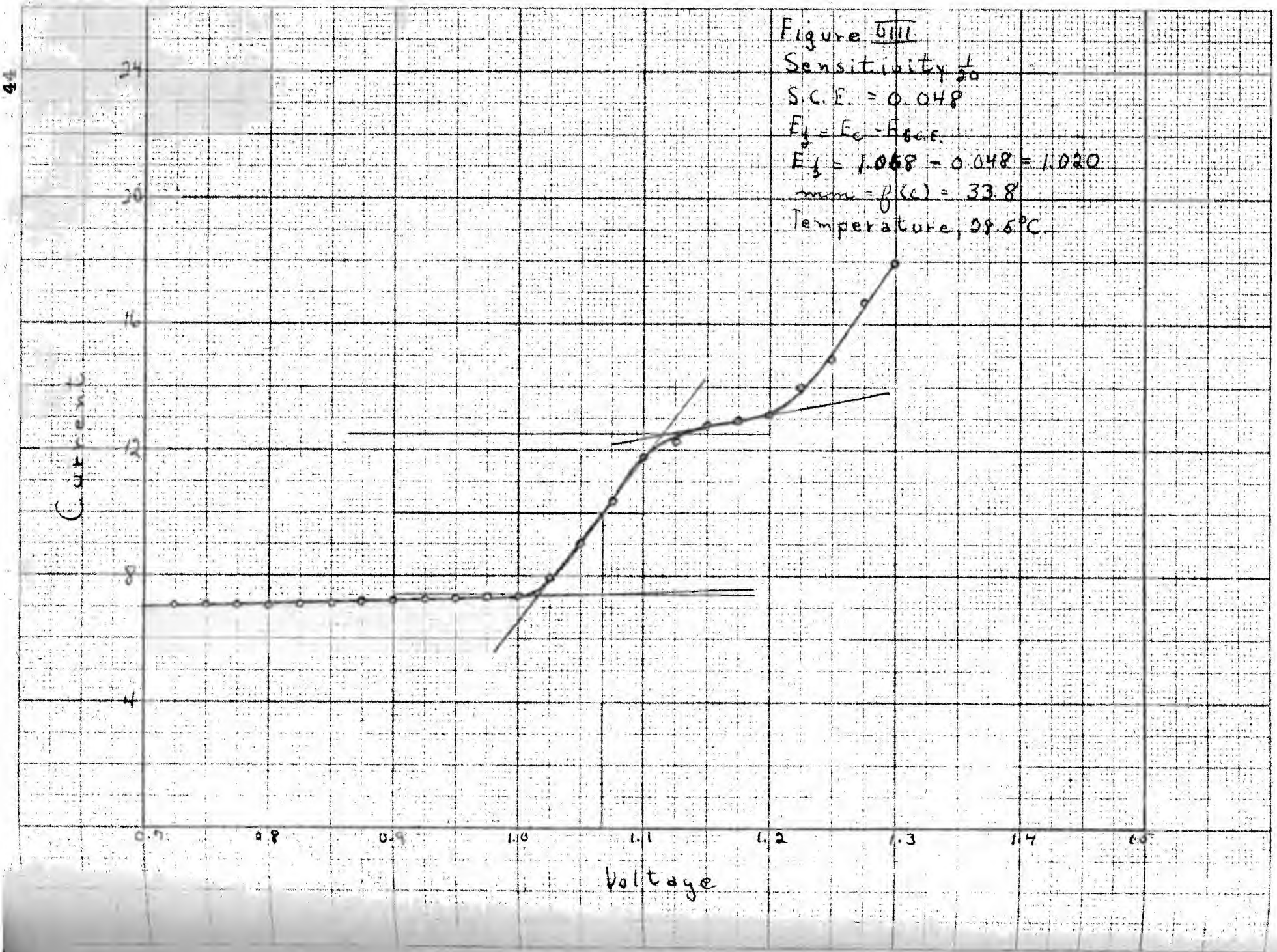
Sensitivity of 1/50

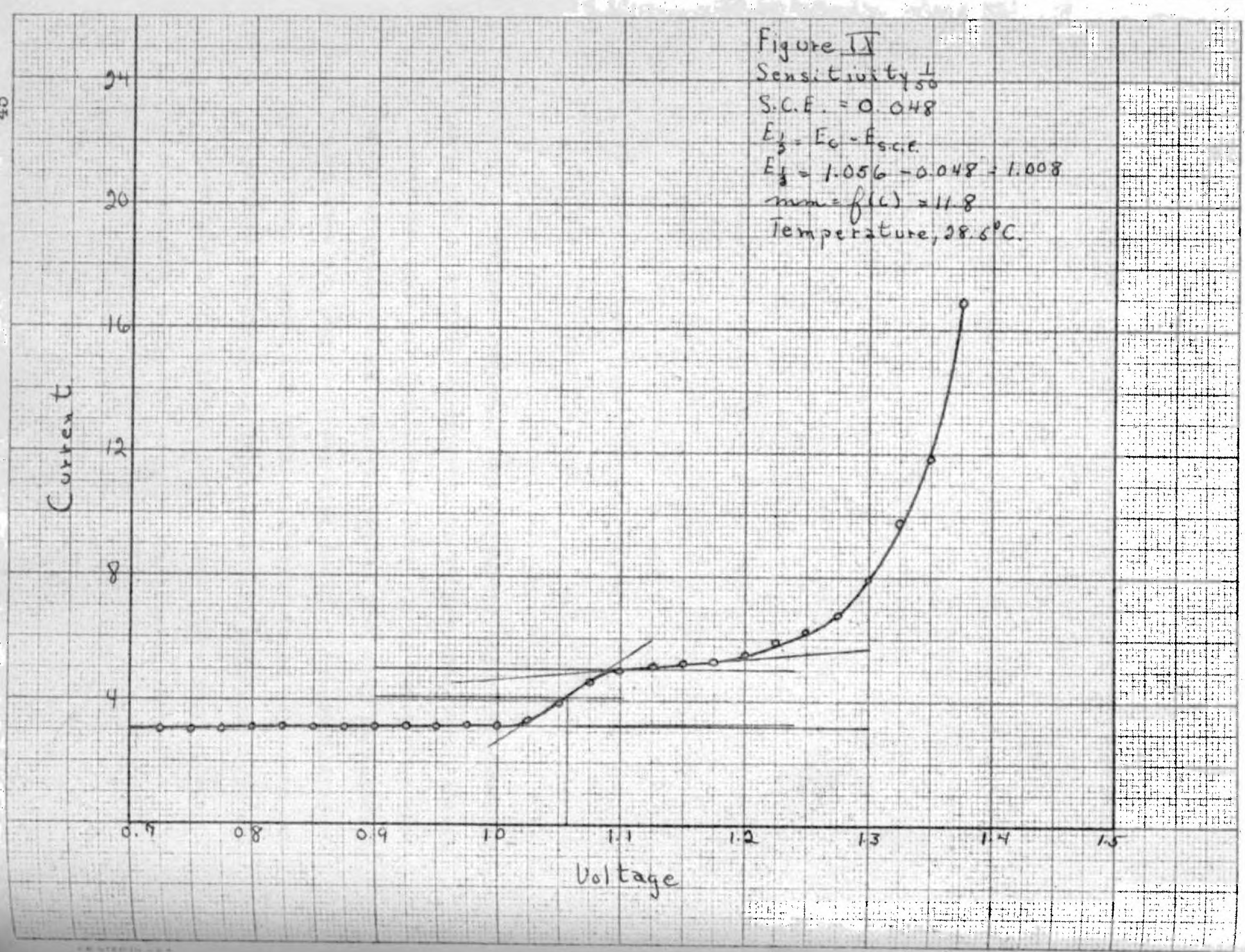
Sample Number	Weight in Grams Sample	Ash	Step Ht. in mm.	Molarity of Sample x 10^{-4}M	Per Cent of Zinc Sample	Ash
2	56.8462	2.9949	13.9	4.75	0.0114	0.216
**3	49.7978	2.6022	5.2	1.85	0.0126	0.243
**4	58.5556	3.0858	5.2	1.85	0.0108	0.204
5	41.1852	2.2163	9.1	3.13	0.0104	0.193
6	55.0438	2.9036	11.8	4.05	0.0100	0.190
*13	47.6608	2.4885	12.0	4.10	0.0129	0.247
14	48.8576	2.6298	11.1	3.83	0.0107	0.199
Average:					0.0113	0.241

*Sample was diluted to 110 cc instead of 100 cc.

**Sample was diluted to 250 cc instead of 100 cc.

Figure VIII
Sensitivity $\frac{1}{20}$
S.C.E. = 0.048
$E_{\frac{1}{2}} = E_c - E_{S.C.E.}$
$E_{\frac{1}{2}} = 1.068 - 0.048 = 1.020$
$i_{max} = \beta(c) = 33.8$
Temperature, 28.6°C.





During the analysis of this variety of soybean considerable difficulty was encountered with the Elecdropode. The capillary used in the previous sample became clogged and could not be cleaned, even with aqua regia. Thus another capillary had to be used; this capillary had the same bore diameter as the first capillary. The current-voltage readings were taken at the same temperature and with the same mercury reservoir height so that the percentage of the last two samples differ slightly from the other samples.

CONCLUSIONS

1. For the first time, the presence of zinc in three varieties of soybeans, Doxi, Rokusun, and Laredo, has been detected.
2. The percentage of zinc in these three varieties has also been found. The percentage of zinc in the Doxi variety is 0.0105 per cent; Rokusun variety 0.0125 per cent; and Laredo variety 0.0110 per cent.
3. The quantity of zinc present in the ash of the three varieties has also been determined for the first time. The Doxi variety contained 0.222 per cent zinc; the Rokusun variety 0.235 per cent; and the Laredo variety 0.222 per cent. The percentage of zinc in the sample of ash was not determined as accurately as the zinc in the sample because of the fact that the ash contained several hygroscopic salts.
4. The polarographic method was found very applicable to the analysis of zinc in soybeans. The method was very accurate because the percentage of zinc in the samples, using two different sensitivities, checked within 1.5 per cent. This slight deviation was not due to the procedure followed, but rather to the difficulty in reading the galvanometer scale accurately to tenths

and in converting the step height to molarity from the standardization curve.

BIBLIOGRAPHY

Easly, H. F., "Rapid Cleaning of Mercury," Industrial and Engineering Chemistry, Analytical Edition, 9:82 (1923)

Fick, A., Poggendroff's Annalen, 94:59 (1855)

Griffin, R. C., Technical Methods of Chemical Analysis, New York: McGraw-Hill Book Company, 1927. 609 pp.

Heyrovsky, J., and Ilkovic, D., "Polarographic Studies with the Dropping Mercury Electrode," Collections of Czechoslovak Chemical Communications, 7:198 - 214 (1935)

_____, and Shikata, M., "Researches with the Dropping Mercury Cathode," Recveil des travaux chimiques des Pays-Bas, 44:496-498 (1925)

Hibbard, B. L., "A Dithizone Method for Measurement of Small Amounts of Zinc," Industrial and Engineering Chemistry, Analytical Edition, 9:127-131 (1937)

_____, "Estimation of Copper, Zinc, and Cobalt in Soil Extracts," Industrial and Engineering Chemistry, Analytical Edition, 10:615-618 (1938)

Kucera, G., "The Surface Potential of Polarized Mercury," Annalen der Physik, 9:529-560 (1903)

Kolthoff, I. M., and Laitinen, H. A., pH and Electro-Titrations, New York: John Wiley and Sons, Inc., 1941. 190 pp.

_____, and Lingane, J. J., "The Fundamental Principles and Applications of Electrolyses with the Dropping Mercury Electrode and Heyrovsky's Polarographic Method of Chemical Analysis," The Chemical Review, 24:1-94

_____, and _____, Polarography, New York: Interscience Publishers, Inc., 1941. 510 pp.

Lloyd, J. W. and Burlison, W. L., Eighteen Varieties of Edible Soybeans, University of Illinois Agricultural Experiment Station Bulletin No. 453: 385-438 (1938)

Lott, W. L., "Determination of Zinc," Industrial and Engineering Chemistry, Analytical Edition, 10: 335-338 (1938)

Mueller, O. H., "Oxidation and Reduction of Organic Compounds at the Dropping Mercury Electrode and the Application of Heyrovsky's polarographic Analysis in Organic Chemistry," The Chemical Review, 24: 95-124 (1939)

_____, The Polarographic Method of Analysis, Easton, Penna.: Mack Printing Company, 1941. 141 pp.

Reed, J. F., and Cummings, R. W., "Determination of Zinc in Plant Materials," Industrial and Engineering Chemistry, Analytical Edition, 10: 489-492 (1940)

Rogers, L. A., and Gall, O. E., "Microdetermination of Zinc," Industrial and Engineering Chemistry, Analytical Edition, 9: 42-44 (1937)

Stout, P. R., Levy, J. and Williams, L. C., "Polarographic Studies with the Dropping Mercury Cathode," Collections of Czechoslovak Chemical Communications, 10: 129-136 (1938)

Polarographic Analysis, Chicago: E. H. Sargent and Company, 1939. 31 pp.

Bibliography of the Polarized Dropping Mercury Electrode, Philadelphia: Leeds and Northrup Company 1941. 68 pp.